Supplementary material

Photodegradation of pesticides using compound-specific isotope analysis (CSIA): a review

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1. Table Classification of pesticides based on category and general remarks

Classification	Category			Remark
Chemical type	AS Arsenic compound OP Organophosphorus compound BP Bipyridylium derivative OT Organotin compound C Carbamate PAA Phenoxyacetic acid derivative CO Coumarin derivative PZ Pyrazole CU Copper compound PY Pyrethroid HG Mercury compound T Triazine derivative NP Nitrophenol derivative TC Thiocarbamate OC Organochlorine compound			These chemical classifications are included only for convenience, and do not represent a recommendation on the part of the World Health Organization for how pesticides should be classified.
Physical state	L denotes liquid: including solids with a melting point below 50°C Oil denotes oily liquids, and S denotes solids including waxes			The physical state may affect the exposure potential, and thus the absorbed amount of the chemical may be considered when determining classification under the previous scheme.
Main use	AC Acaricide L Larvicide AP Aphicide M Molluscicide B Bacteriostat (soil) MT Miticide FM Fumigant N Nematocide F Fungicide, other than for seed O Other use for plant pathogens treatment PGR Plant growth regulator FST Fungicide, for seed treatment R Rodenticide H Herbicide RP() Repellant (species) I Insecticide -S applied to soil: not used with herbicides IGR Insect growth regulator or plant growth regulators Ix Ixodicide (for tick control) SY Synergist			In most cases only a single use is given. This is only for identification purposes and does not exclude other uses.
"The Globally Harmonized System of Classification and Labelling of Chemicals" (GHS)[1]		LD$_{50}$ [a] (mg/kg bw)	LD$_{50}$ [b] (mg/kg bw)	The GHS table shows only a simplified summary. For full classification details according to the GHS, the official publication of the GHS should be consulted.
LD50	Category 1	<5	<50	a) For oral data, the rat is the preferred species, though data from other species may be appropriate when scientifically justified.
	Category 2	5–50	50–200	
	Category 3	50–300	200–1000	

	Category 4	300–2000	1000–2000	b) For dermal data, rats or rabbits are the preferred species, though data from other species may be appropriate when scientifically justified.
	Category 5	2000–5000	2000–5000	

Bw represents “body weight”.

2. Calculation of compound stable isotope analysis

Stable isotope analysis measures the natural isotopic composition of the target element in the molecule of a compound and is expressed by the heavy to light isotope ratio (e.g., $^{13}C/^{12}C$, $^{2}H/^{1}H$, $^{15}N/^{14}N$). This isotopic composition can often be used as a fingerprint for a particular compound identification.[2] The stable isotope ratio (R) is usually expressed as a relative value in parts per thousand, relative to the international standard substance, as shown by equation (1):

$$R\left(\frac{^{\mathrm{h}}E}{^{l}E}\right)_c = \frac{N(^{\mathrm{h}}E)_c}{N(^{l}E)_c} \quad (1)$$

N_c, number of entities of a compound, $R_{E,}$ isotopic ratio of element E, and ^{h}E and ^{l}E, relative percentage atomic content of heavy and light isotopes of element E. Because comparing the light and heavy isotope values according to abundance results in values too low for comparison, the δ scale $\delta^{h}E_c$ of a compound is defined as the relative deviation of the isotopic ratio R $(^{h}E/^{l}E)_C$ of an element in the sample (e.g. $^{2}H/^{1}H$ or $^{13}C/^{12}C$) from the isotopic ratio R $(^{h}E/^{l}E)$ref of a standard sample. This is shown in equation (2):

$$\delta^{\mathrm{h}}E_{c,ref} = \left[\frac{R(^{\mathrm{h}}E/^{l}E)_c}{R(^{\mathrm{h}}E/^{l}E)_{ref}} - 1\right] \times 10^3 \quad (2)$$

where the reference material is the international standard material, positive and negative δ values are used to indicate the enrichment and depletion of the heavy isotopes of specific elements in the sample relative to the international standard. By this a visual representation of the isotopic composition of each measurement point can be represented. The δ value of an elemental stable isotope is often expressed as a ratio in thousandths of a percent (‰); for example, δ^{13}Cbenzene = −0.0284 for benzene, and then using equation (2), $\delta^{13}C_{benzene}$ = −28.4‰. In general, a positive δ value indicates a higher ratio of heavy isotopes to light isotopes in a sample compared to the standard, whereas the opposite is true for a negative δ value. For example, a sample with an isotopic ratio of δ^{13}C of +5‰ indicates a higher value than the international standard by 0.5‰, which is equivalent to a $^{13}C/^{12}C$ value of 0.0112361, compared to the isotopic ratio of 0.0111802 for the standard. Therefore, +0.005 or +5‰ would be multiplied by 1000‰.

The Rayleigh equation (3) was used to find a relationship between the change in the isotopic composition and degree of degradation, according to:

$$\ln\left(\frac{Rx,t}{Rx,0}\right) = \varepsilon_{bulk} \cdot \ln f \quad (3)$$

where ε_{bulk} is the isotopic enrichment factor observed for the compound, f is the fraction of degradation (often described as C/C_0, where C_0 and C are the concentrations of the compound at times zero and t, respectively), and Rx is the isotopic composition of the elements (carbon or bromine) in the substrate at times zero and t.

The isotopic enrichment factor, ε_{bulk}, was obtained as a slope of the linear regression line of the natural logarithm of the isotopic enrichment, $R_{x,t}/R_{x,0}$, versus the natural logarithm of the extent of degradation, f.

The kinetic isotope effect (KIE) during pollutant conversion leads to an enrichment in the δ values of the heavier isotopes in the remaining products. KIE is a physical phenomenon that occurs when molecules with lighter isotopes in the chemical bonds, specifically in chemical reactions that usually react more rapidly than those with heavier isotopes during chemical reactions, result in an enrichment of the heavier isotopes and are enriched in the parent compound. Meanwhile, the lighter isotopes are more enriched in the resulting products. The kinetic isotope effect can be calculated by:

$$KIE = {}^{1}\!/\!\left(1 + \varepsilon_{bulk}\right) \quad (4)$$

where ε_{bulk} represents the $\varepsilon_{reactive}$ position, and the actual isotope effect on the reacting carbon is diluted by the non-reacting carbons. The $\varepsilon_{Creactive}$ position was calculated according to the following equation:

$$\varepsilon_{Creact.\,pos.} = n \cdot \varepsilon_{bulk} \quad (5)$$

where *n* is the total number of *C* atoms in the molecule.

Apparent kinetic isotope effects were calculated according to equation 6:[3]

$$AKIE = 1/(1 + \varepsilon_{Creact.pos.}) \quad (6)$$

3. Using CSIA to estimate bioavailability

According to the Rayleigh equation, the relationship between the stable isotope ratio ($\delta^{13}C$) and compound concentration during a biodegradation reaction is $\frac{R_t}{R_0} = \left(\frac{\frac{c_t}{c_0}}{\frac{R_{t+1}}{R_{0+1}}}\right)^{\varepsilon}$. The relationship between residual pesticide concentration Ct and the concentration of pesticides not available to microorganisms due to ageing behavior and sorption in soil (b) can be calculated according to the bioavailable fraction $BA = \frac{c_{t-b}}{c_t}$. Combining these two equations, $\frac{R_t}{R_0} = \left(\frac{\frac{c_t}{c_0}}{\frac{R_{t+1}}{R_{0+1}}}\right)^{\varepsilon}$ and $BA = \frac{c_{t-b}}{c_t}$, we can assume the equation $BA = 1 - \frac{b}{c_0 * \left[(1 + \delta_t^{13}C)/(1 + \delta_0^{13}C)\right]^{1/\varepsilon}}$, which reveals the bioavailable fraction of pesticides as determined by CSIA.

4. Magnetic field isotope effect (MIE)

MIE is defined as the mass-independent isotope effect, resulting from the interaction of the magnetic field associated with electron spin, and the magnetic field associated with nuclei spin.

In an excited state chemical reaction, two radical pairs (radical pairs, RPs) with weakly interacting spin states (single linear S & triple linear T) are formed by the excited molecules. Radical pairs with different spin states exhibit obvious differences in nature, such as different bond lengths, spatial molecule configurations, and electron distributions, resulting in distinctly different physical and chemical properties, and thus different products can be generated in excited state chemical reactions. The smaller energy difference between the monoclinic and trilinear radical pairs thus allows the magnetic field to influence the interlinear scurry between the monoclinic and trilinear states, which ultimately affects the reaction rate and product yield of the excited state chemical reactions. The magnetic interaction of electrons is an excited state photophysical process, and the protonation state of the organic contaminants and the position of the aromatic substituents can influence the photolysis reaction to produce different reaction mechanisms.

The radical pairs containing magnetic nuclei undergo spin conversion and recombination with the starting molecule much faster than nonmagnetic spin nuclei. Furthermore, MIE usually appears in the form of steps in the chemical reaction and they do not limit the rate of the overall process.[4]

5. References

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